Alma L. Coats et al.

10/628,304

Filing Date: Page 2 of 15 July 29, 2003

Amendments to the claims

This listing of claims will replace all prior versions and listings of the claims.

Attorney Docket No.:

14974.0002

Listing of Claims:

1.- 29. (Canceled).

- 30. (Currently amended) A liquid stereolithography resin comprising a first urethane acrylate oligomer, a first acrylate monomer, a polymerization modifier, a second urethane acrylate oligomer different from the first urethane acrylate oligomer, and a stabilizer; wherein the first urethane acrylate oligomer is an aliphatic polyester urethane diacrylate oligomer, an aliphatic urethane acrylate oligomer, an aliphatic urethane containing bound silicone, or an aromatic urethane acrylate oligomer, wherein the first acrylate monomer is ethoxylated (3) trimethylolpropane acrylate, and the polymerization modifier is selected from the group consisting of isobornyl acrylate, ethoxylated (5) pentaerythritol tetraacrylate, an aliphatic urethane acrylate, tris-(2-hydroxyethyl)isocyanurate triacrylate, and mixtures thereof, wherein the resin includes 5-35 weight % an aliphatic polyester urethane diacrylate oligomer and 0.5-25 weight % ethoxylated (3) trimethylolpropane acrylate, The liquid stereolithography resin of claim 28, wherein the resin includes 15-45 weight % ethoxylated (5) pentaerythritol tetraacrylate.
- 31. (Currently amended) A liquid stereolithography resin comprising a first urethane acrylate oligomer, a first acrylate monomer, a polymerization modifier, a second urethane acrylate oligomer different from the first urethane acrylate oligomer, and a stabilizer; wherein the first urethane acrylate oligomer is an aliphatic polyester urethane diacrylate oligomer, an aliphatic urethane acrylate oligomer, an aliphatic urethane containing bound silicone, or an aromatic urethane acrylate oligomer, wherein the first acrylate monomer is ethoxylated (3) trimethylolpropane acrylate, and the polymerization modifier is selected from the group consisting of isobornyl acrylate, ethoxylated (5) pentaerythritol tetraacrylate, an aliphatic urethane acrylate, tris-(2-hydroxyethyl)isocyanurate triacrylate, and mixtures thereof, wherein the resin includes 5-35 weight % an aliphatic polyester urethane diacrylate oligomer and 0.5-25

Alma L. Coats et al.

Application No.: Filing Date:

10/628,304

Page 3 of 15

July 29, 2003

weight % ethoxylated (3) trimethylolpropane acrylate, The liquid stereolithography resin of elaim 28, wherein the resin includes 0.5-25 weight % an aliphatic urethane acrylate.

Attorney Docket No.:

14974.0002

- (Withdrawn—currently amended) The liquid stereolithography resin of claim 30 32. +, wherein the resin includes 5-35 weight % tris-(2-hydroxyethyl)isocyanurate triacrylate.
- (Withdrawn—currently amended) The liquid stereolithography resin of claim 30 33. 4, wherein the first urethane acrylate oligomer is an aliphatic urethane acrylate oligomer, the first acrylate monomer is tripropyleneglycol diacrylate, and the polymerization modifier is selected from the group of CN970H75, ethoxylated (4) bisphenol A dimethyacrylate, isobornyl-acrylate, and mixtures thereof.

34-36. (Canceled).

- (Withdrawn—currently amended) The liquid stereolithography resin of claim 34 37. 30, wherein the resin includes 5-35 weight % isobornyl acrylate.
- (Withdrawn—currently amended) The liquid stereolithography resin of claim + 38. 30, wherein the first urethane acrylate oligomer is an aliphatic polyester urethane diacrylate oligomer, the first acrylate monomer is isobornyl acrylate, and the polymerization modifier is selected from the group consisting of isobornyl acrylate, ethoxylated (4) bisphenol A dimethyacrylate, and mixtures thereof.
- 39. (Withdrawn—currently amended) The liquid stereolithography resin of claim 38 30, wherein the resin includes 10-40 35 weight % an aliphatic polyester urethane diacrylate and 0.5-25 weight % isobornyl acrylate.
- (Withdrawn—currently amended) The liquid stereolithography resin of claim 38 40. 30, wherein the resin includes 6-35 weight % isobornyl acrylate.

Alma L. Coats et al.

10/628,304

Filing Date: Page 4 of 15

July 29, 2003

polydimethylsiloxane, and mixtures thereof.

41. (Canceled).

42. (Withdrawn—currently amended) The liquid stereolithography resin of claim 1 30, wherein the first urethane acrylate oligomer is an aliphatic urethane containing bound silicone, the first acrylate monomer is isobornyl acrylate, and the polymerization modifier is selected from the group consisting of CN131, a polyether modified acryl functional

Attorney Docket No.:

14974.0002

43. (Withdrawn—currently amended) The liquid stereolithography resin of claim 42 30, wherein the resin includes 50-80 weight % an aliphatic urethane containing bound silicone and 0.5-20 weight % isobornyl acrylate.

44-45. (Canceled).

- 46. (Withdrawn—currently amended) The liquid stereolithography resin of claim 4 30, wherein the first urethane acrylate oligomer is an aromatic urethane acrylate oligomer, the first acrylate monomer is isobornyl acrylate, and the polymerization modifier is isobornyl acrylate.
- 47. (Withdrawn—currently amended) The liquid stereolithography resin of claim 46 30, wherein the resin includes 45-75 weight % an aromatic urethane acrylate oligomer and 10-70 weight % isobornyl acrylate.

48-50. (Canceled).

51. (Withdrawn—currently amended) The liquid stereolithography resin of claim 49 30, wherein the resin includes 10-40 weight % isobornyl acrylate.

52-55. (Canceled).

Alma L. Coats et al.

Application No.:

10/628,304

Filing Date: Page 5 of 15 July 29, 2003

56. (Currently Amended) The A liquid stereolithography resin of claim 30 comprising: wherein the a first urethane acrylate oligomer having has formula (I):

$$A - O = \underbrace{\left(M^{1} - O\right)_{x}^{O} \frac{O}{H} - M^{2} - N - \frac{O}{H} - O}_{x} + \underbrace{\left(M^{1} - O\right)_{z}^{2} A}_{y}$$
 (I)

Attorney Docket No.:

14974.0002

wherein

each M¹ is, independently, an alkylene, an acylalkylene, an oxyalkylene, an arylene, an acylarylene, or an oxyarylene, M¹ being optionally substituted with alkyl, cycloalkyl, alkenyl, cycloalkenyl, alkynyl, acyl, alkoxy, hydroxyl, hydroxylalkyl, halo, haloalkyl, amino, silicone, aryl, or aralkyl,

each M² is, independently, an alkylene or an arylene, M² being optionally substituted with alkyl, cycloalkyl, alkenyl, cycloalkenyl, alkynyl, acyl, alkoxy, hydroxyl, hydroxylalkyl, halo, haloalkyl, amino, silicone, aryl, or aralkyl,

each A, independently, has the a formula:

wherein R¹ is hydrogen or lower alkyl, each L is, independently, C₁-C₄ alkyl, and w is an integer ranging from 0 to 20, and

x is a positive integer less than 40, y is a positive integer less than 100, z is a positive integer less than 40, and w, x, y, and z together are selected such that the molecular weight of the first urethane acrylate oligomer is less than 20,000;

a first acrylate monomer having formula (II):

$$A'-O-R^2-(O-A')_n \qquad (II)$$

wherein

R² is a monovalent or polyvalent moiety selected from the group consisting of a C₁-C₁₂ aliphatic group, an aromatic group, and a poly(C1-C4 branched or unbranched alkyl ether), R2 being optionally substituted with alkyl, cycloalkyl, alkenyl, cycloalkenyl, alkynyl, acyl, alkoxy, hydroxyl, hydroxylalkyl, halo, haloalkyl, amino, aryl, or aralkyl,

n is an integer ranging from 0 to 5, and

Alma L. Coats et al.

Application No.: Filing Date:

10/628,304

Page 6 of 15

July 29, 2003

each A' has the a formula:

$$-(L-O)_{w} \bigcap_{R^{1}}^{O}$$

wherein R¹ is hydrogen or lower alkyl, each L independently is C₁-C₄ alkyl, and w is an integer ranging from 0 to 20; and

Attorney Docket No.:

14974.0002

a polymerization modifier selected from the group consisting of isobornyl acrylate, ethoxylated (5) pentaerythritol tetraacrylate, an aliphatic urethane acrylate, tris-(2hydroxyethyl)isocyanurate triacrylate, and mixtures thereof including a second urethane acrylate oligomer different from the first urethane acrylate oligomer and a stabilizer.

(Currently amended) The liquid stereolithography resin of claim 56, further 57. comprising a photoinitiator and a stabilizer.

58-68. (Cancelled)

- (Currently amended) The liquid stereolithography resin of claim 4 30, further 69. comprising a photoinitiator.
- 70. (Previously presented) The liquid stereolithography resin of claim 69, wherein the photoinitiator includes a phosphine oxide, an alpha-hydroxyketone, and a benzophenone derivative.
- (Previously presented) The liquid stereolithography resin of claim 69, wherein 71. the photoinitiator includes a component selected from the group consisting of a benzophenone, a benzil dimethyl ketal, a 1-hydroxy-cyclohexylphenylketone, an isopropyl thioxanthone, an ethyl 4-(dimethylamino)benzoate, a blend of 2,4,6-trimethylbenzoyldiphenyl phosphine oxide, 2,4,6trimethylbenzophenone, 4-methylbenzophenone, and oligo(2-hydroxy-2-methyl-1-(4-(1methylvinyl)phenyl)propanone, a benzoin normal butyl ether, a blend of oligo(2-hydroxy-2methyl-1-(4- (1-methylvinyl)phenyl) propanone) and poly(2-hydroxy-2-methyl-1-phenyl-1-

Alma L. Coats et al.

Application No.: Filing Date:

10/628,304 July 29, 2003

Page 7 of 15

)/628,304

propanone), tripropyleneglycol diacrylate, an oligo(2-hydroxy-2-methyl-1-(4-(1-methylvinyl)phenyl)propanone), a 2-hydroxy-2-methyl-1-phenyl-1-propanone, a poly(2-hydroxy-2-methyl-1-phenyl-1-propanone), a trimethylolpropane triacrylate, a mixture of 2,4,6-trimethylbenzophenone and 4-methylbenzophenone, a phosphine oxide, a 4-methylbenzophenone, a trimethylbenzophenone, a methylbenzophenone, and a blend of 2,4,6-trimethylbenzoyl-diphenyl-phosphineoxide and hydroxy-2-methyl-1-phenyl-propan-1-one.

Attorney Docket No.:

14974.0002

- 72. (Previously presented) The liquid stereolithography resin of claim 69, wherein the photoinitiator includes a component selected from the group consisting of a blend of 2,4,6-trimethylbenzoyl-diphenyl-phosphineoxide and hydroxy-2-methyl-1-phenyl-propan-1-one, a phosphine oxide, a 2-hydroxy-2-methyl-1-phenyl-1-propanone, and mixtures thereof.
- 73. (Previously presented) The liquid stereolithography resin of claim 69, wherein the photoinitiator activates polymerization of an acrylate in a wavelength range of 240 nm to 250 nm, 360 nm to 380 nm, or 390 nm to 410 nm.

74-78. (Canceled).

- 79. (Currently amended) The liquid stereolithography resin of claim <u>30</u> 78, wherein the stabilizer is selected from the group consisting of (bis(1,2,2,6,6-pentamethyl-4-piperidyl)sebacate and 1-methyl-10-(1,2,2,6,6-pentamethyl-4-piperidyl)sebacate), (bis(1,2,2,6,6-pentamethyl-4-piperidyl)sebacate), MEQH (4-methoxyphenol), 2-(2'-hydroxy-5'-methylphenyl)benzotriazole, 1,2,2,6,6-pentamethyl-4-piperidyl methacrylate and (2-hydroxy-4-octyloxybenzophenone).
 - 80. (Canceled).
- 81. (Currently amended) A liquid stereolithography resin comprising an aliphatic polyester urethane diacrylate oligomer, an ethoxylated (3) trimethylolpropane acrylate, and a polymerization modifier comprising a member selected from the group consisting of isobornyl

Alma L. Coats et al.

Application No.: Filing Date:

10/628,304

Page 8 of 15

July 29, 2003

acrylate, ethoxylated (5) pentaerythritol tetraacrylate, an aliphatic urethane acrylate, tris-(2hydroxyethyl)isocyanurate triacrylate, and mixtures thereof, The liquid stereolithography resin of claim 68, wherein the resin includes 15-45 weight % ethoxylated (5) pentaerythritol tetraacrylate.

Attorney Docket No.:

14974.0002

- (Currently amended) A liquid stereolithography resin comprising an aliphatic 82. polyester urethane diacrylate oligomer, an ethoxylated (3) trimethylolpropane acrylate, and a polymerization modifier comprising a member selected from the group consisting of isobornyl acrylate, ethoxylated (5) pentaerythritol tetraacrylate, an aliphatic urethane acrylate, tris-(2hydroxyethyl)isocyanurate triacrylate, and mixtures thereof, The liquid stereolithography resin of claim 68, wherein the resin includes 0.5-25 weight % an aliphatic urethane acrylate.
 - 83. (Canceled).
- 84. (New) The liquid stereolithography resin of claim 31, wherein the resin includes 5-35 weight % tris-(2-hydroxyethyl)isocyanurate triacrylate.
- 85. (New) The liquid stereolithography resin of claim 31, wherein the first urethane acrylate oligomer is aliphatic urethane acrylate oligomer.
- 86. (New) The liquid stereolithography resin of claim 31, wherein the resin includes 5-35 weight % isobornyl acrylate.
- (New) The liquid stereolithography resin of claim 31, wherein the first urethane 87. acrylate oligomer is an aliphatic polyester urethane diacrylate oligomer.
- (New) The liquid stereolithography resin of claim 31, wherein the resin includes 88. 10-35 weight % an aliphatic polyester urethane diacrylate and 0.5-25 weight % isobornyl acrylate.

Alma L. Coats et al.

Application No.: 10/628,304

Filing Date:

July 29, 2003

Page 9 of 15

89. (New) The liquid stereolithography resin of claim 31, wherein the resin includes 6-35 weight % isobornyl acrylate.

Attorney Docket No.:

14974.0002

- 90. (New) The liquid stereolithography resin of claim 31, wherein the first urethane acrylate oligomer is an aliphatic urethane containing bound silicone.
- 91. (New) The liquid stereolithography resin of claim 31, wherein the resin includes 50-80 weight % an aliphatic urethane containing bound silicone and 0.5-20 weight % isobornyl acrylate.
- 92. (New) The liquid stereolithography resin of claim 31, wherein the first urethane acrylate oligomer is an aromatic urethane acrylate oligomer.
- (New) The liquid stereolithography resin of claim 31, wherein the resin includes 93. 45-75 weight % an aromatic urethane acrylate oligomer and 10-70 weight % isobornyl acrylate.
- 94. (New) The liquid stereolithography resin of claim 31, wherein the resin includes 10-40 weight % isobornyl acrylate.
- (New) The liquid stereolithography resin of claim 31, wherein the a first urethane 95. acrylate oligomer has formula (I):

$$A-O = \left(M^{1}-O \right)_{x} \frac{O}{H} - M^{2}-N \frac{O}{H} - O = O \left(M^{1}-O \right)_{z} A \qquad (I)$$

wherein

each M¹ is, independently, an alkylene, an acylalkylene, an oxyalkylene, an arvlene, an acylarylene, or an oxyarylene, M¹ being optionally substituted with alkyl, cycloalkyl, alkenyl, cycloalkenyl, alkynyl, acyl, alkoxy, hydroxyl, hydroxylalkyl, halo, haloalkyl, amino, silicone, aryl, or aralkyl,

each M² is, independently, an alkylene or an arylene, M² being optionally substituted with

Alma L. Coats et al.

Application No.: Filing Date:

10/628,304 July 29, 2003

Page 10 of 15

Attorney Docket No.:

14974.0002

alkyl, cycloalkyl, alkenyl, cycloalkenyl, alkynyl, acyl, alkoxy, hydroxyl, hydroxylalkyl, halo, haloalkyl, amino, silicone, aryl, or aralkyl,

each A, independently, has a formula:

$$-(L-O)_{w}^{O}$$

wherein R¹ is hydrogen or lower alkyl, each L is, independently, C₁-C₄ alkyl, and w is an integer ranging from 0 to 20, and

x is a positive integer less than 40, y is a positive integer less than 100, z is a positive integer less than 40, and w, x, y, and z together are selected such that the molecular weight of the first urethane acrylate oligomer is less than 20,000;

a first acrylate monomer having formula (II):

$$A'-O-R^2-(O-A')_0$$
 (II)

wherein

R² is a monovalent or polyvalent moiety selected from the group consisting of a C₁-C₁₂ aliphatic group, an aromatic group, and a poly(C₁-C₄ branched or unbranched alkyl ether), R² being optionally substituted with alkyl, cycloalkyl, alkenyl, cycloalkenyl, alkynyl, acyl, alkoxy, hydroxyl, hydroxylalkyl, halo, haloalkyl, amino, aryl, or aralkyl,

n is an integer ranging from 0 to 5, and each A' has a formula:

wherein R¹ is hydrogen or lower alkyl, each L independently is C₁-C₄ alkyl, and w is an integer ranging from 0 to 20; and

a polymerization modifier selected from the group consisting of isobornyl acrylate, ethoxylated (5) pentaerythritol tetraacrylate, an aliphatic urethane acrylate, tris-(2-hydroxyethyl)isocyanurate triacrylate, and mixtures thereof.

Alma L. Coats et al.

10/628,304

Filing Date:

July 29, 2003

Page 11 of 15

(New) The liquid stereolithography resin of claim 95, further comprising a 96. photoinitiator.

Attorney Docket No.:

14974.0002

- 97. (New) The liquid stereolithography resin of claim 31, further comprising a photoinitiator.
- 98. (New) The liquid stereolithography resin of claim 97, wherein the photoinitiator includes a phosphine oxide, an alpha-hydroxyketone, and a benzophenone derivative.
- 99. (New) The liquid stereolithography resin of claim 97, wherein the photoinitiator includes a component selected from the group consisting of a benzophenone, a benzil dimethyl ketal, a 1-hydroxy-cyclohexylphenylketone, an isopropyl thioxanthone, an ethyl 4-(dimethylamino)benzoate, a blend of 2,4,6-trimethylbenzoyldiphenyl phosphine oxide, 2,4,6trimethylbenzophenone, 4-methylbenzophenone, and oligo(2-hydroxy-2-methyl-1-(4-(1methylvinyl)phenyl)propanone, a benzoin normal butyl ether, a blend of oligo(2-hydroxy-2methyl-1-(4- (1-methylvinyl)phenyl) propanone) and poly(2-hydroxy-2-methyl-1-phenyl-1propanone), tripropyleneglycol diacrylate, an oligo(2-hydroxy-2-methyl-1-(4-(1methylvinyl)phenyl)propanone), a 2-hydroxy-2-methyl-1-phenyl-1-propanone, a poly(2hydroxy-2-methyl-1-phenyl-1-propanone), a trimethylolpropane triacrylate, a mixture of 2,4,6trimethylbenzophenone and 4-methylbenzophenone, a phosphine oxide, a 4methylbenzophenone, a trimethylbenzophenone, a methylbenzophenone, and a blend of 2,4,6trimethylbenzoyl-diphenyl-phosphineoxide and hydroxy-2-methyl-1-phenyl-propan-1-one.
- (New) The liquid stereolithography resin of claim 97, wherein the photoinitiator 100. includes a component selected from the group consisting of a blend of 2,4,6-trimethylbenzoyldiphenyl-phosphineoxide and hydroxy-2-methyl-1-phenyl-propan-1-one, a phosphine oxide, a 2hydroxy-2-methyl-1-phenyl-1-propanone, and mixtures thereof.

Alma L. Coats et al.

10/628,304

Page 12 of 15

July 29, 2003

Filing Date:

(New) The liquid stereolithography resin of claim 97, wherein the photoinitiator 101. activates polymerization of an acrylate in a wavelength range of 240 nm to 250 nm, 360 nm to 380 nm, or 390 nm to 410 nm.

Attorney Docket No.:

14974.0002

(New) The liquid stereolithography resin of claim 31, wherein the stabilizer is 102. selected from the group consisting of (bis(1,2,2,6,6-pentamethyl-4-piperidyl)sebacate and 1methyl-10-(1,2,2,6,6-pentamethyl-4-piperidyl)sebacate), (bis(1,2,2,6,6-pentamethyl-4piperidyl)sebacate), MEQH (4-methoxyphenol), 2-(2'-hydroxy-5'-methylphenyl)benzotriazole, 1,2,2,6,6-pentamethyl-4-piperidyl methacrylate and (2-hydroxy-4-octyloxybenzophenone).